

# Liquid-Phase Oxidation of Benzene to Phenol by Molecular Oxygen over La Catalysts Supported on HZSM-5

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**Abstract** The liquid-phase oxidation of benzene to phenol over lanthanum oxide catalysts (LaO<sub>x</sub>/HZSM-5) supported on HZSM-5 was studied in the presences of oxygen as an oxidant and ascorbic acid as a reducing reagent. LaO<sub>x</sub>/HZSM-5 effectively catalyzes the formation of phenol at 353 K under the pressurization of oxygen. The LaO<sub>x</sub>/HZSM-5 catalysts take place no leaching of lanthanum species from the catalysts to acidic solvent. Therefore, it is demonstrated that the supported lanthanum catalysts are stable and reusable for the benzene oxidation even in the acidic reaction solution.

**Keywords** Lanthanum · Partial oxidation of Benzene · Phenol synthesis · HZSM-5

## 1 Introduction

The partial oxidation of hydrocarbons into various derivatives such as alcohols, aldehydes, ketones, carboxylic acids and epoxides has been extensively investigated, because such products are industrially significant [1–5].

However, the industrial oxidation process usually demands high selectivities, high yields, energy efficiency or economical efficiency. Phenol production, which is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics, is currently carried out through the Cumene process or toluene oxidation. Especially, former process which is a most popular process of phenol production consists of three steps and produces acetones as byproduct. The direct oxidation of benzene is more desirable for the phenol production, because of more economical and without byproducts.

The liquid-phase direct hydroxylation of benzene has been reported by Dixon and Norman using ferrous sulfate-H<sub>2</sub>O<sub>2</sub> system (Fenton reagent) [6]. The partially exchanged hetero-poly acid has been also reported as a catalyst for the liquid-phase oxidation of benzene in the presence of H<sub>2</sub>O<sub>2</sub> oxidation [7, 8]. It has been more recently studied that molecular oxygen directly oxidizes benzene to phenol on various catalysts in the presence of reducing reagent [9–14]. We have reported that supported copper or vanadium catalysts effectively oxidize the benzene in acetic acid solution into phenol with molecular oxygen in the presence of ascorbic acid as a reducing reagent, however, the leaching of copper or vanadium species on the support is a serious problem [11–14].

Alkali metals added to the supported lanthanum catalysts effectively catalyze the partial oxidation of benzyl alcohol into benzaldehyde in the gas-phase reaction [15]. We have proposed that the alkali metals added to the supported lanthanum catalysts may activate the gaseous oxygen for the partial oxidation activity because of having a low activity for the partial oxidation without the lanthanum. Hence, it seems that lanthanum in the catalysts plays a significant role of partial oxidation. In this study, we detail the direct liquid-phase oxidation of benzene to

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phenol over lanthanum oxide catalysts supported on HZSM-5 in the presence of oxygen and reducing reagent.

## 2 Experimental

HZSM-5 was supplied by ZEOLYST (CBV8014: Si/Al = 43, BET surface area = 425 m<sup>2</sup>/g, Na<sub>2</sub>O < 0.05 wt%). Lanthanum oxide supported on HZSM-5 was prepared by impregnation using an aqueous solution of La(CH<sub>3</sub>COO)<sub>3</sub>·1.5H<sub>2</sub>O (Nacalai Tesuque, extra pure reagent). The solvent was removed by heating at ca. 360 K. The supported lanthanum catalysts were dried at 393 K overnight and calcined at 773 K for 5 h in flowing air. The sample will be designated as *n* wt% LaO<sub>x</sub>/HZSM-5 where *n* represents the content of lanthanum (*n* = 0.2~1.0).

The liquid-phase oxidation of benzene was carried out using a stainless steel reactor (Taiatsu glass, i.d.: 1.7 cm; height: 11.2 cm) with a magnetic stirrer. The standard reaction condition is as follows: 0.1 g of catalyst, 5 cm<sup>3</sup> of aqueous solvent containing prescribed amount of acetic acid, 5.6 mmol (0.5 cm<sup>3</sup>) of benzene, 1 mmol of ascorbic acid, 0.4 MPa of oxygen, reaction temperature of 353 K, and reaction time 24 h. After adding 5 cm<sup>3</sup> of 2-propanol as an internal standard to the reaction solution, the reaction solution which was separated from the solid catalyst by centrifugation were analyzed by gas chromatograph equipped with a Flame Ionization detector (Shimadzu GC-8A) with a nitrogen carrier gas. 2-Propanol was conformed not to convert to acetone during the treatment. The amounts of La in the leaching

solution were also estimated by analysis of an inductively coupled plasma (ICP) emission spectra (Seiko Instruments SPS1500VR).

## 3 Results and Discussion

Table 1 shows the yield of phenol for the benzene oxidation over several LaO<sub>x</sub>/HZSM-5 catalysts. Phenol effectively formed over 0.5 wt% LaO<sub>x</sub>/HZSM-5 catalysts under the oxygen pressure at 0.4 MPa and the temperature at 353 K. We have previously reported that lanthanum supported catalysts effectively oxidized benzyl alcohol into benzaldehyde [15]. Hence, the lanthanum supported catalysts may effectively catalyze partial oxidation of hydrocarbon. No leaching of lanthanum species from the catalysts to the reaction solvent was observed during the oxidation. The used catalysts led to the decrease in the phenol formation in comparison with the fresh catalysts, because the recovery of the used catalyst from the reaction solution caused a loss. The activities per a gram of catalyst for the both catalysts were almost same. These results indicate that the LaO<sub>x</sub>/HZSM-5 catalysts are reusable and stable for this reaction.

As shown in Table 1, the reaction which carried out under the reaction pressure at 0.1 MPa took place the lower formation of phenol. It is speculated that the lower reaction pressure of O<sub>2</sub> leads to the lack of oxidant in the reaction solution. The small amount of phenol formation also proceeds even without catalysts. (see Table 1) The absence of oxygen or ascorbic acid took place no formation of phenol

**Table 1** Catalytic performance for the benzene oxidation into phenol under the different conditions

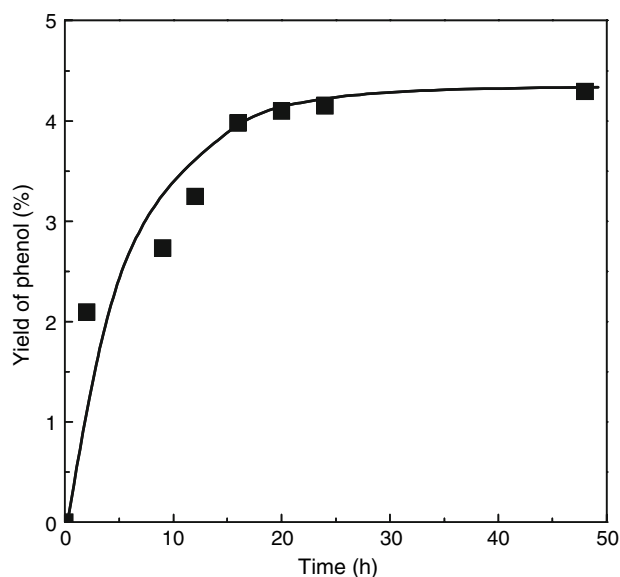
Catalyst	Concentration of acetic Acid (%)	Yield of phenol (%)	Leaching of La (%)	BET (m <sup>2</sup> /g)
No catalyst	80	1.5	—	—
HZSM-5	80	1.5	—	402
0.2 wt% LaO <sub>x</sub> /HZSM-5	80	2.2	0	356
0.5 wt% LaO <sub>x</sub> /HZSM-5	80	3.0	0	325
1.0 wt% LaO <sub>x</sub> /HZSM-5	80	2.9	0	293
1.0 wt% LaO <sub>x</sub> /HZSM-5 <sup>a</sup>	80	0.4	0	293
0.5 wt% LaO <sub>x</sub> /HZSM-5	70	4.2	0	325
0.5 wt% LaO <sub>x</sub> /HZSM-5 <sup>b</sup>	70	3.3	0	293
0.5 wt% LaO <sub>x</sub> /HZSM-5 <sup>c</sup>	70	3.6	0	293

Experimental conditions: 0.1 g catalyst, 0.5 cm<sup>3</sup> (5.6 mmol) of benzene, 1 mmol of ascorbic acid, 5 cm<sup>3</sup> of aqueous acetic acid solvent, reaction pressure at 0.4 MPa of oxygen, reaction temperature at 353 K

<sup>a</sup> Reaction carried out under the reaction pressure at 0.1 MPa and reaction temperature at 303 K

<sup>b</sup> Reaction carried out on the reused catalyst (0.091 g) which was separated from reaction solvent by centrifugation after 1st reaction and dried at 393 K overnight

<sup>c</sup> Reaction carried out on the reused catalyst (0.085 g) which was separated from reaction solvent by centrifugation after 2nd reaction and dried at 393 K overnight



**Fig. 1** The time profile of phenol yields for the oxidation of benzene over 0.5 wt%  $\text{LaO}_x/\text{HZSM-5}$  in the presence of ascorbic acid and oxygen at 0.4 MPa at 353 K

over the lanthanum oxide catalysts. It seems that the molecular oxygen and reducing reagents in the reaction solution play a significant role in this reaction system.

The time profile of phenol yields for the oxidation of benzene over 0.5 wt%  $\text{LaO}_x/\text{HZSM-5}$  catalyst is shown in Fig. 1. The increase of the phenol yield for this reaction was observed until 20 h, and that rate gradually decreased with the advance of reaction. No formation of phenol was observed after reaction time at 20 h. The re-addition of

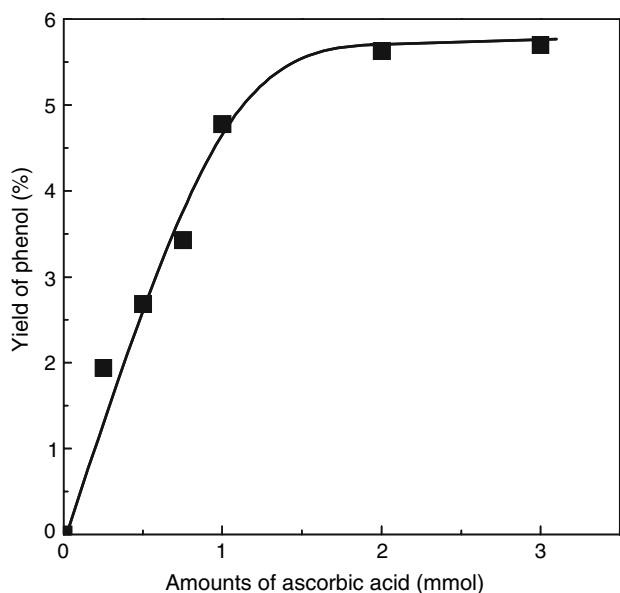
ascorbic acid after the reaction caused further formation of phenol. Hence, we speculate that the inactivation of phenol formation is brought by the consumption of reducing reagent in the reaction system. Figure 2 indicates about the effect of amounts of ascorbic acid on the phenol yields. The increase of amounts of ascorbic acid leads to the increase of phenol yields until the addition at 2 mmol. Although, the excess amounts of reducing reagents did not accelerate the further formation of phenol. The excess presence of ascorbic acid may lead to the self-decompose of reducing reagents or the formation of inhibitor.

In summary, lanthanum oxide supported on HZSM-5 effectively catalyzes the oxidation of benzene with molecule oxygen and ascorbic acid to phenol in the liquid-phase reaction. No leaching of lanthanum species from the catalysts to the acidic solution is observed. The absence of an oxidant or a reducing reagent takes place no formation of phenol. The addition of excess amounts of a reducing reagent leads to the inactivation of benzene oxidation, considering due to the self-decompose of reducing reagents or the formation of inhibitor. Although a detailed mechanism will be the subject of future work, we can emphasize that the  $\text{LaO}_x/\text{HZSM-5}$  which are reusable and stable effectively function as a catalyst for the liquid-phase oxidation of benzene to phenol.

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**Fig. 2** Yields of phenol for the oxidation of benzene over 0.5 wt%  $\text{LaO}_x/\text{HZSM-5}$  for 24 h at 353 K and 0.4 MPa  $\text{O}_2$  with various amount of ascorbic acid